SYNTHESIS OF SOME SUBSTITUTED STYRENES

BY

DELTON WILLIAM HEIN

A. B., University of South Dakota, 1939

M. S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

SYNTHESIS OF SOME SUBSTITUTED STYRENES

Introduction

GR-S, the synthetic rubber most widely used for the production of vehicle tires during the natural rubber shortage, has certain defects which cause it to be inferior to natural rubber in some properties. Considerable effort has been made to correct these defects. One method of attack has been to determine the effect of replacing the styrene in GR-S with certain substituted styrenes. In a continuation of this program, *p*-benzylstyrene, *o*-methoxystyrene, and *o*-fluorostyrene have been prepared and copolymerized with butadiene in quantities sufficient to permit a laboratory evaluation of the copolymers. Bis-(*p*-vinylphenyl)-methane has been prepared and submitted for evaluation as a cross-linking agent in synthetic rubber.

Discussion of Results

p-Benzylstyrene was prepared from diphenylmethane which was synthesized from benzyl chloride and benzene according to the method outlined in Organic Syntheses[1]. *p*-Benzylacetophenone was prepared by the acetylation of diphenylmethane according to the Perrier modification of the Friedel-Crafts' method as used by Mowry, Renoll, and Huber[2]. Some bis-(*p*-acetylphenyl)methane was produced in each run. The reduction of *p*-benzylacetophenone with hydrogen in the presence of Raney nickel gave 1-(*p*-benzylphenyl)-ethanol, which was dehydrated over activated alumina by the procedure of Mowry, Renoll, and Huber[2] to give *p*-benzylstyrene.

Bis-(*p*-vinylphenyl)methane was prepared from the bis-(*p*-acetylphenyl)methane obtained as a by-product in the *p*-benzylacetophenone synthesis. Reduction of this diketone with hydrogen in the presence of Raney nickel catalyst gave bis-[*p*-(1-hydroxyethyl)phenyl]methane, which was also de-

hydrated over activated alumina by the procedure of Mowry, Renoll, and Huber[2] to form bis-(*p*-vinylphenyl)methane.

o-Methoxystyrene was prepared by four methods. First it was prepared from *o*-anisaldehyde which was synthesized by the methylation of salicylaldehyde according to the Organic Syntheses' procedure[1] for the methylation of vanillin. *o*-Anisaldehyde was converted to 1-(*o*-methoxyphenol)ethanol by treatment with methylmagnesium iodide, and this carbinol was dehydrated by the same procedure used for the preparation of *p*-benzylstyrene. The product failed to copolymerize with butadiene in a standard recipe[3]. Since it was thought that the product might contain an impurity peculiar to the method of synthesis, it was prepared from *o*-bromoanisole. *o*-Bromoanisole was converted to the Grignard reagent, and it was treated with acetaldehyde to give 1-(*o*-methoxyphenyl)-ethanol which was dehydrated in the same manner as above. The product failed to copolymerize with butadiene, which appeared to indicate that the impurities, which acted as inhibitors, were being formed in the alumina dehydration reaction. Therefore 2-(*o*-methoxyphenyl)ethanol was prepared from *o*-bromoanisole and ethylene oxide by the Grignard reaction. This carbinol was dehydrated over hot potassium hydroxide pellets. The *o*-methoxystyrene produced copolymerized satisfactorily with butadiene. Since sufficient *o*-bromoanisole was not immediately available to prepare enough *o*-methoxystyrene for evaluation, it was prepared from *o*-anisaldehyde essentially by the method of Walling and Wolfstirn[4]. *o*-Anisaldehyde was condensed with malonic acid in the presence of pyridine to give *trans*-*o*-methoxycinnamic acid. This acid was decarboxylated by the distillation of its quinoline solution in the presence of copper powder. The *o*-methoxystyrene produced copolymerized satisfactorily with butadiene if an alkaline wash was included in the purification procedure of Walling and Wolfstirn[4] to remove the *o*-methoxycinnamic acid which distilled.

o-Fluorostyrene was also prepared from *o*-fluorobenzalde-

hyde by the general method of Walling and Wolfstirn[4]. *o*-Fluorotoluene was prepared from *o*-toluidine hydrochloride by the Organic Syntheses' procedure[1] for the preparation of fluorobenzene. *o*-Fluorotoluene was converted to *o*-fluorobenzaldehyde by the Organic Syntheses' procedure[1] for the preparation of *p*-bromobenzaldehyde. *o*-Fluorobenzaldehyde was condensed with malonic acid in the presence of pyridine. Decarboxylation of the *o*-fluorocinnamic acid was affected by the distillation of its quinoline solution in the presence of copper.

The *p*-benzylstyrene produced by the alumina dehydration reaction was shown to contain *p*-benzylethylbenzene. The *o*-methoxystyrene produced by the same method was shown to contain about 10 per cent *o*-ethylphenol and an appreciable quantity of *o*-ethylanisole. The *o*-methoxystyrene made in this way failed to copolymerize with butadiene. When washed thoroughly with alkali and carefully distilled, it copolymerized with butadiene but the conversions were always low and the copolymer was soft and tacky. The same behavior[5] was shown by 3,4-dimethoxystyrene produced by alumina dehydration. *p*-Phenoxystyrene produced by the same reaction was shown[5] to contain *p*-phenoxyethylbenzene. Arylethane contamination might be responsible for the low intrinsic viscosities of the GR-S type copolymers obtained from substituted styrenes prepared by this reaction, since the benzyl hydrogens might act as chain transfer agents and thus behave as modifiers. Since the substituted styrene and the corresponding arylethane are very difficult to separate by distillation, it would appear that the alumina dehydration procedure, as used by Mowry, Renoll, and Huber[2], is unsuitable for the preparation of pure styrenes for evaluation purposes.

Bis-(*p*-vinylphenyl)methane was submitted for evaluation as a cross-linking agent in GR-S type copolymers. Its polymer and that of each of the substituted styrenes was made by ultra-violet light catalysis. Copolymers of each

styrene were made by emulsion copolymerization with butadiene according to a standard recipe[3]. These copolymers were submitted for industrial evaluation.

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VITA

The author was born September 5, 1916, in Webster, South Dakota. He attended the public schools in Webster, South Dakota, and was graduated from high school in June, 1935. He entered the University of South Dakota in September, 1935, and received the Bachelor of Arts degree in Chemistry in June, 1939. He enrolled in the Graduate School of the University of Illinois in September, 1939, and held a graduate assistantship from that time until February, 1942. He received the Master of Sciences degree in 1941. He worked as a research assistant for the National Defense Research Committee Toxicity Laboratory at the University of Chicago from February 1 to July 1, 1942. He was ordered to active duty in the military service as a second lieutenant on July 7, 1942, and was assigned to duty with the Technical Division of the Office of the Chief, Chemical Warfare Service (later renamed the Chemical Corps) in Washington, D. C. On December 7, 1942, he was assigned to duty with the Chemical Warfare Service Technical Command at the Chemical Warfare Center, Edgewood Arsenal, Maryland. He was promoted to the rank of first lieutenant on August 28, 1942, to the rank of captain on May 11, 1943, and to the rank of major in the Chemical Corps Reserve on January 23, 1947. He was separated from the military service on January 21, 1946. He returned to graduate study at the University of Illinois in March, 1946, and has been employed since that time as a special research assistant in chemistry on the Rubber Research Program.

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